

PREPARATION OF NEW LAYERED DOUBLE HYDROXIDE, Co-V LDH

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Received: March 23, 2005

Abstract. The layered double hydroxide (LDH) is well known for its ability to intercalate anionic compounds. Most popular LDH is prepared conventionally only with divalent and trivalent cations. In this study, Co-V LDH consisting of divalent and tetravalent cations was prepared and reacted with monocarboxylic acids at room temperature. The Co-V LDH and intercalated compounds characterized by C,H,N analysis, ICP, ESCA, X-ray diffraction, IR spectra, thermal analysis and Scanning electron microscope (SEM). XRD patterns of the prepared Co-V LDH showed that the interlayer spacing of the LDH is 0.78 nm. SEM images showed that the morphology of Co-V LDH before and after intercalation reactions is plate-like structure.

1. INTRODUCTION

Nano structured inorganic-organic or hybrid organic-inorganic nano composites will contribute to the development of science and technology. Layered double-metal hydroxides (LDHs) are one of the nano ordered layered compounds.

An increasing interest exists in layered double-metal hydroxides [1-6], which are or may be used as catalysts, photo catalysts, catalyst supports adsorbents, anion exchangers, medicine and bonding materials.

Layered double hydroxides (LDHs) are anionic clays comprising positively charged layers with anions and water molecules intercalated in the interlayer region [1]. The best known compound in this class of materials is the double hydroxide of Mg with Al, known as hydrotalcite [1]. We call these the II-III LDHs. In case of using Li with Al, some researchers [7] succeeded to prepare layered double hydroxide call I-III LDH. Although several examples of II-III LDHs are reported, Li-Al LDH is the only known example of I-III LDH. Attempts by the authors to

prepare Fe, Cr and Ga analogues failed to yield LDHs with Li [8].

Novel methods for generating vanadium oxide layers on supports are the area of active research. For instance, Dredzon *et al.* [9] have reported the ion exchange of vanadate anion into the layered double hydroxide. Rives *et al.* [10] reported the formation of II-III layered double hydroxide containing Mg²⁺ and V³⁺ ions or Ni²⁺ and V³⁺ ions in the layers.

We recently reported that the preparation of Zn-Ti and Co-Ti LDH consisting of di- and tetra-valent cations are possible [11,12]. The present work examines the possibility of preparation of other example consisting of di- and tetra-valent cations LDH. This new LDH structure contains Co²⁺ and V⁴⁺ cations in host layers and cyanate and carbonate anions as the guests. The effect of aging time on the formation of LDH structure was clarified.

2. EXPERIMENTAL

Materials. The Co-V LDH was prepared by co-precipitation of cobalt and vanadium salts from homo-

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geneous solution [11, 12]. A solution of cobalt nitrate and vanadyl dichloride (VOCl_2) were mixed with urea solution under vigorous stirring and heated for long time.

The percentage of vanadium is 22 mole%. After filtration and washing several times in distilled water, the products were dried under vacuum at room temperature.

Intercalation. Typically, appropriate amount of sodium salt of organic acid (0.002 moles) dissolved in 10 ml of deionized - distilled water (concentration about 0.2M) with ultrasonic treatment. The LDH (0.24 g) was mixed with the solution of organic acid under Ar atmosphere and stirred at room temperature for 72 h. After filtration and washing, the samples were dried under vacuum at room temperature.

Characterization. Chemical analyses were obtained with a Perkin Elmer CHNS/O 2400II analyzer. Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using $\text{CuK}\alpha$ (filtered) radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 20 mA between 1.8 and 50° . Thermal analysis (TG, DTG and DTA) of powdered samples up to 800°C were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ in flow of nitrogen using a Seiko SSC 5200 apparatus. FT-IR spectra (KBr disc method) were recorded on a Horiba FT-720. Scanning electron microscopy (SEM) was performed with JEOL: JSM-6330F, (15 kV/12 mA).

3. RESULTS AND DISCUSSIONS

Chemical Analysis of Co-V LDH. The chemical analysis, elemental analysis (as determined by ICP) and electron spectroscopy for chemical analysis (ESCA) suggest the structure of Co-V LDH as shown in the formulae:



This formulae suggests that the Co-V LDH contain cyanate and carbonate anions as guests.

X-ray Diffraction. The X-ray diffraction patterns of Co-V LDH are given in Fig. 1. The measured XRD pattern of Co-V LDH fits well to layered structure with no evidence for other phases. The X-ray diffraction of Co-V LDH (Fig. 1) shows the basal peaks of planes hkl (003), (006) and (009). The good agreement between the values corresponding to successive diffractions by basal planes, i.e. $d(003) = 2d(006) = 3d(009)$ for Co-V LDH, reveals highly packed stacks of brucite-like layers ordered along axis c. Dimension c is calculated as three times the spacing for planes (003), i.e. 2.34 nm. The c dimension is very close to that reported for natural and synthetic hydroxide, 2.31 nm [13]. The XRD pattern of Co-V

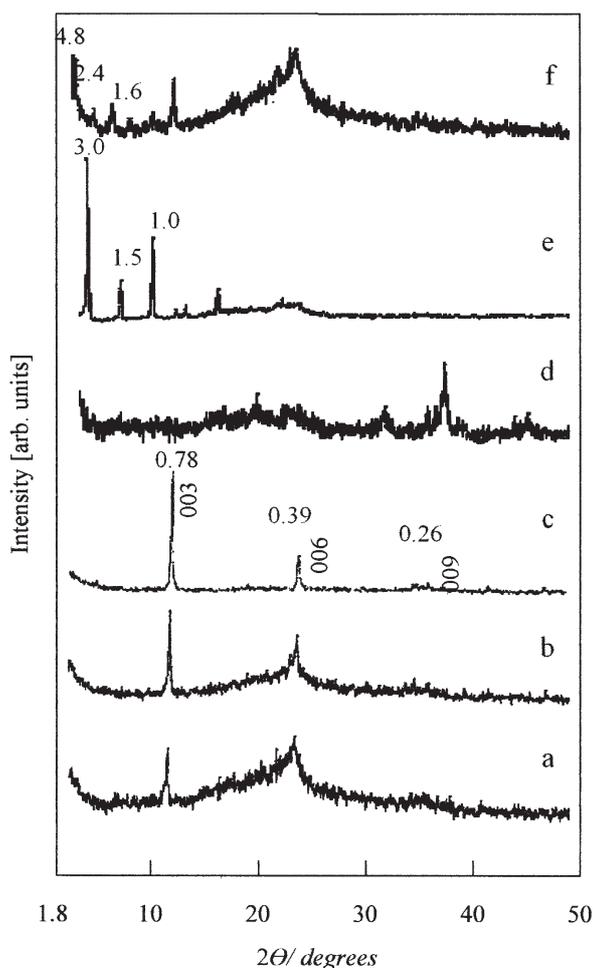


Fig. 1. X-ray diffraction patterns of Co-V LDH with aging time (a) 6 h, (b) 8 h, (c) 16 h, (d) after calcinations at 500°C and after intercalation reactions with (e) *n*-capric acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$) and (f) stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$).

LDH has the main peak at 0.78 nm, which corresponded to interlayer spacing of the LDH as shown in Fig. 1.

The peaks of layered structure disappeared by the calcination at 500°C , and appearance of new peaks at high 2θ values as shown in Fig. 1d indicates the formation of metal oxides.

By the reaction of Co-V LDH with *n*-capric acid at room temperature, new peaks were observed at low 2θ indicating interlayer spacing 3.0 nm as shown in Fig. 1e. Also, by the treatment of Co-V LDH with longer organic acid, stearic acid, new peaks were observed at lower 2θ indicating interlayer spacing 4.8 nm as shown in Fig. 1f. This suggests that the Co-V LDH could perform intercalation reactions with organic acid.

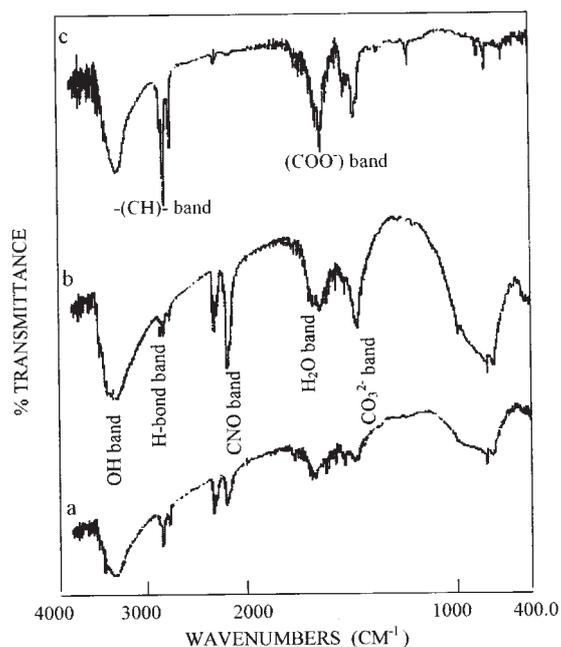


Fig. 2. IR Spectra of Co-V LDH (a) at 6 h, (b) at 16 h and (c) after intercalation reaction with *n*-capric acid.

FT-IR Spectroscopy. The FT-IR technique has been used to identify the nature and symmetry of interlayer anions. The insertion of cyanate anion (NCO⁻) into Co-V LDH is very easily demonstrated by the appearance of the ν_1 vibration in the 2230-2105 cm^{-1} region, the ν_2 vibration in the 600-650 cm^{-1} region and the ν_3 vibration in the 1190-1220 cm^{-1} region of the infrared spectrum of the materials [14]. As can be noted in Figs. 2a and 2b, the carbonate anion and hydroxyl group are confirmed by a clear absorption peak at 1383 cm^{-1} and broad peak at 3500 cm^{-1} , respectively [14].

A weak peak recorded around 2856 cm^{-1} has been ascribed to the OH stretching mode of interlayer water molecules hydrogen-bonded to interlayer carbonate and cyanate anions [15]. The bending mode band of water molecules observed close to 1637 cm^{-1} [16]. These results indicate that the Co-V LDH has similar structure with usual LDH structure and it confirms the presence of carbonate anions and cyanate anions in addition to water molecules inside the interlayer space.

Also, the existence of organic compound into Co-V LDH after intercalation reactions confirmed by the results of IR spectroscopy as shown in Fig. 2c. In the IR spectrum of the reaction products of Co-V

LDH with straight chain of aliphatic acid such as *n*-capric acid, the carbon-hydrogen stretch absorption at near 2900 cm^{-1} and the carbon-hydrogen bending band at 1470 cm^{-1} were observed as shown in Fig. 2c. Also, the new peaks at near 1540 and 1400 cm^{-1} appeared. The absorption at 1540 cm^{-1} is assigned to the symmetric stretching vibration of carboxylate, and the absorption at 1400 cm^{-1} is assigned to the asymmetric stretching vibration of carboxylate. On the other hand, the carbonate and cyanate anions disappeared.

Thermal analysis. Thermal characteristics of the Co-V LDH in nitrogen gas were determined by TG, DTG and DTA. Major losses of weight occur mainly in three steps. The TG diagram showed that the first weight loss up to 90 °C is 9% and the second weight loss up to 207 °C is 11.5%. The main weight loss occurs from 207 °C to 500 °C in two steps. The first step corresponds to the decomposition of cyanate anion and the second step due to the decomposition of carbonate anions and dehydroxylation process. These steps confirmed from DTG and DTA diagrams.

DTA diagram show three endothermic peaks. The first peak at around 50 °C corresponds to the desorption of surface water, the second at 252 °C corresponds to the decomposition of cyanate anions and the third peak at 290 °C corresponds to the decomposition of carbonate and dehydroxylation of layers. These processes, (decomposition of cyanate, decomposition of carbonate and dehydroxylation of layers) are clearly distinguished when the analysis is performed in air instead of in nitrogen.

The TG of Co-V LDH in air showed that the main weight loss occurred in three steps indicating three processes. Also, the DTA of Co-V LDH in air showed two exothermic peaks accompanied with the main weight loss. These exothermic peaks due to the oxidation of cyanate anion, Co²⁺ and V⁺⁴ cations. This agrees with ESCA analysis that confirmed the presence of cobalt as divalent cation and vanadium as tetravalent.

TG and DTG curves of monocarboxylic acids alone and Co-V intercalation compounds of them indicated that decomposition temperature of monocarboxylic acids shifted to higher temperatures by intercalation. These results suggest occurrence of the intercalation reactions.

Scanning electron microscope (SEM). SEM images of Co-V LDH before and after intercalation reactions are shown in Fig. 3. SEM image of Co-V LDH show a clear plate-like morphology which was typical for the LDH morphology as shown in Fig.

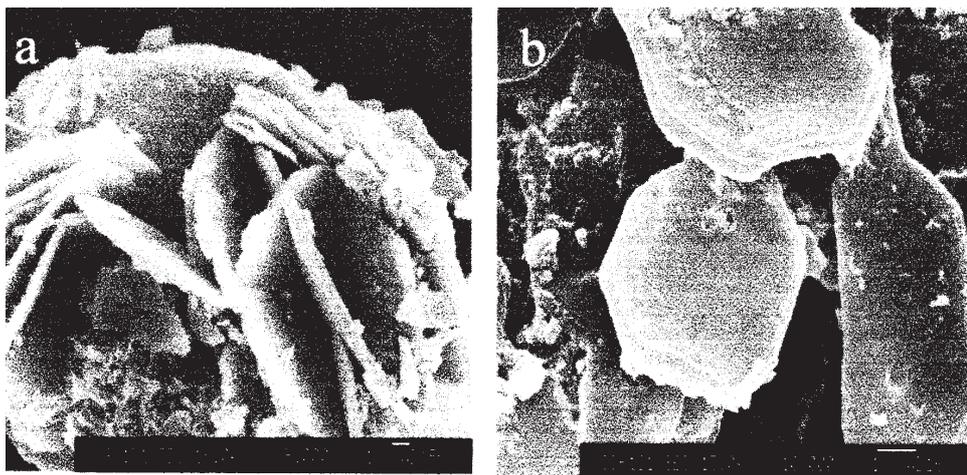


Fig. 3. SEM images of (a) Co-V LDH and (b) Co-V LDH after reaction with *n*-capric acid.

3a. The intercalation compounds of Co-V LDH also show a clear plate-like morphology indicating that the average size of the organic compounds containing crystallites is much larger than that for the samples before intercalation reactions as shown in Fig. 3b.

4. DISCUSSION

The results presented in this work show that the formation of the layer double hydroxide is not limited to the reactions between di- and trivalent cations although these are the only reactions reported by many researchers [1-6]. The powder XRD patterns are not sufficiently high quality to allow us to carry out structure determination. However, by interlayer spacing and the size of the guest ions, orientation of guest ions was considered. From known layer thickness, 0.48 nm, the interlayer spacing available for the anion was calculated as 0.30 nm. By comparison with the size of cyanate anion, 0.34 nm, it was considered that cyanate anion make an angle 65.7° with the Co-V layer and connect with V cation through two different sides (above and below the layer) in order to neutralize the positive charge as shown in Fig. 4.

The experimental results show that two anions are intercalated into the interlayer spacing of Co-V LDH indicating one interlayer spacing 0.78 nm.

The first anion, mainly intercalated, is cyanate which produced from the decomposition of urea as shown in Eq. (1):



The earlier investigators [17] confirmed this equation and consider that the ammonium cyanate is an intermediate with decomposition of urea. Recently, Coebel *et al.* [18] mentioned that the thermal decomposition of urea can yield a variety of products; apart from ammonia and isocyanic acid.

The second anion is carbonate, which produced from the complete decomposition of urea as shown in Eq. (2):

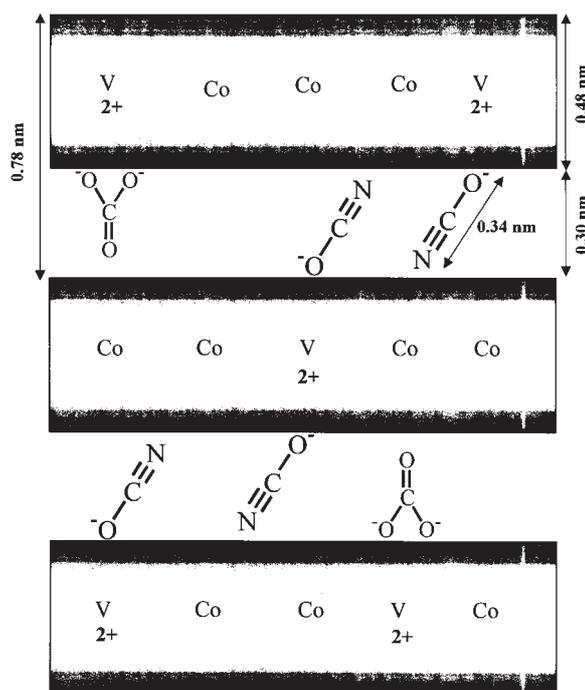
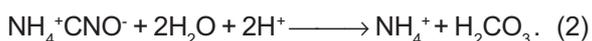


Fig.4. Schematic representation of Co-V LDH.



The earlier investigators [17] indicated that the decomposition of urea is complete only in acidic conditions as shown in Eq. 2.

5. CONCLUSION

In this study, Co-V layered double hydroxides consisting of divalent and tetravalent have been prepared for the first time. The Co-V LDH has interlayer spacing 0.78 nm. SEM images show that the Co-V LDH containing inorganic or organic anions exist as plate-like morphology. Anion-exchange reactions were successful in replacing inorganic anions with organic anions into Co-V LDH.

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